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Influence of Ag doping on Optical Properties of Nanocrystalline Titanium Dioxide prepared by PLD

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Abstract: *In this work, Silver Ag doped nanocrystalline titanium dioxide TiO_2 films deposited with different concentration of $(TiO2)_{1-x}(Ag)_x$ of x= (0, 0.01, 0.02, 0.03, 0.04 and 0.05) Wt. on glass substrates were prepared by pulsed laser deposition (PLD) method, using pulsed Nd-YAG laser with wavelength (λ=1064 nm) and duration (9ns) and energy (700 mJ).The research has been including the study of optical properties through measuring the specters of absorbance and transmittance of the wavelength range (320-1100)nm. The results have been showed that the films have high transmittance for all films around 60-94% in the visible region and NIR of the spectrum that we can use them as optical windows in solar cells.The results of has been showed the absorption coefficient the direct transition are controlled, The values of the energy gap are calculated of the allowed direct electronic transitions are (3.81-3.63)eV. The energy gap is decreased gradually whenever the impurities rate increases.*

Keywords: *optical properties, silver, titanium dioxide films, PLD.*

I. Introduction

Titanium dioxide (TiO_2) has become one of the most researched semiconductor materials due to the great promise it has shown in the photocatalytic oxidation of organic minerals [1-3]. The basic mechanism is the creation of an electron-hole pair by exciting an electron from the valence to the conduction band through light absorption that exceeds the band gap energy [4-5].

Among the numerous oxide materials, titanium dioxide (TiO_2) has received unprecedented interest due to its superior physical, chemical properties, high stability and ability to be easily doped with active ions. This material was used for various optical applications such as high refractive index component of multilayer optical filter, gas sensors, antireflective coating, photocatalysts, and planar waveguides [6]. Due to a combination of such unique properties as high refractive index, high transmittance, chemical stability and photo-catalytic behavior, titanium dioxide constitutes a very valuable material for optical applications [7]. In recent years, many efforts have been directed toward shifting the optical sensitivity of the TiO_2 from UV to the visible-light spectrum for the efficient use of solar radiation or artificial visible light [8]. It is generally agreed that the presence of metal or nonmetal dopants into TiO_2 lattice increases the photocatalytic activity of the mater under visible light irradiation [9-12]. On the other side, producing porous TiO_2 samples with large surface area can improve its photocatalytic properties by means of reducing the recombination rate of photo induced electron-hole pairs. This is due to their faster arrival to the reaction site of the surface and efficient charge separation which increases the lifetime of the charge carriers and enhances the photocatalytic efficiency [13]. The aim of this work is to produce high-quality Ag -dopedTiO_2 thin films for optical application by PLD. Special attention was paid to the influence of the processing parameters, such as dopant concentration into the targets on the optical properties of the films during the deposition.

II. Experiment

Ag-doped TiO_2 thin films were synthesized by pulsed laser deposition system. Thin films were grown in a vacuum chamber generally in ($4x10^{-2}$ mbar) vacuum conditions. The Nd:YAG laser was operated at the wavelength of (λ=1064 nm) with the repetition rate of (6Hz) and pulse duration of (9 ns). The target to substrate distance was (2cm). Targets of pure TiO_2 and Ag-doped TiO_2 films x= (0, 0.01, 0.02, 0.03, 0.04 and 0.05) Wt. Thin films were grown in Oxygen environment with O_2 partial pressure of 10^{-2} mbar at substrate temperature of 250 C. The absorption spectra of undoped and Ag-dopedTiO_2 thin films were studied by UV-visible-NIR (Perkin Elemer Company) spectrophotometer in spectral range of (320-1100) nm.

III. Results and Discussion

The optical Transmission spectra of the nanocrystalline TiO_2 and $(TiO2)_{1-x}(Ag)_x$ films were measured in the region of (320-1100nm) by using UV-VIS-NIR spectrometer at room temperature, fig.(1) shows the optical transmission spectra at various Ag contents for nanocrystalline $(TiO2)_{1-x}(Ag)_x$ films deposited on glass substrate. It is also found that the average transmittance of the $(TiO2)_{1-x}(Ag)_x$ films exceeded 94% at x = 0. This

indicates that TiO_2 film can be used as a window material in solar cells [14]. The transmission values of Ag NPs doped TiO2 thin films (1 %, 2 %, 3%, 4 % and 5 %) are respectively. It is observed that the optical transmittance decreases with increasing the Ag contents this is consistent with the increase of the surface roughness promoting the increase of the surface scattering of the light. Both densification and agglomeration of the crystallites at the doping are responsible for this behavior. The lack of oscillations in the range of 320-1100 nm indicates that the samples are very thin, according to the results obtained by **A. P. Caricatoa, et al**[15].

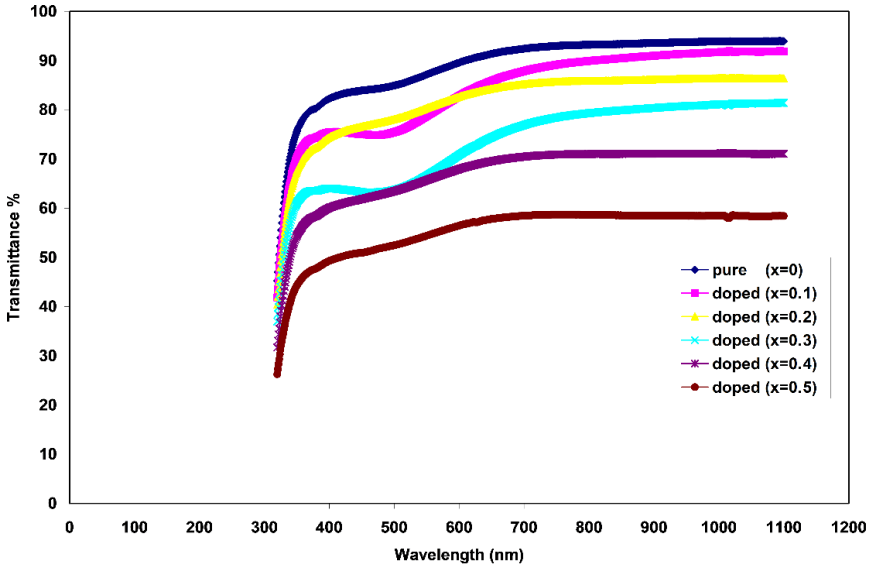

Figure (1): transmittance as a function of wavelength for $(TiO2)_{1-x}(Ag)_x$ films deposited on glass substrate with different Ag contents.

The optical absorbance spectra of the nanocrystalline TiO_2 and $(TiO2)_{1-x}(Ag)_x$ thin films, as shown in fig. (2). It is clear that the absorption edge was shifted to visible region due to Ag doping. In other words, Ag doping causes decreasing in band gap energy, which is the minimum energy to promote the excited electron from valence band to conduction band. The more Ag content, the higher wavelength absorption. A similar trend was also observed in **Lan Sun, et al.(2009)** and**He, et al. (2002*).*** Both studies concluded that the absorption edge shift possibly linked to the interaction of silver and TiO_2[16,17].

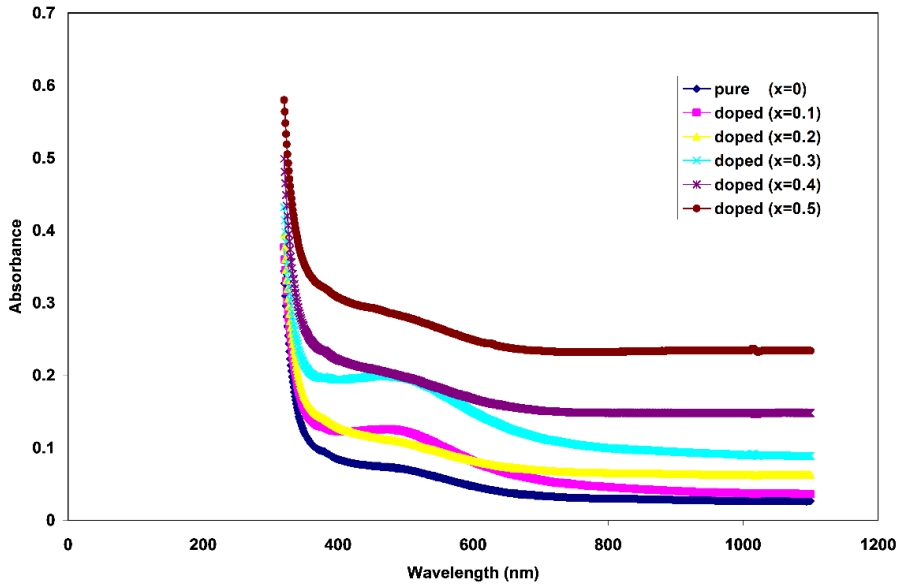

Fig. (2): absorbance spectra as a function of wavelength for $(TiO2)_{1-x}(Ag)_x$ films deposited on glass substrate with different Ag contents.

Fig. (3) shows the absorption coefficient (α) as a function of photon energy of the $\mathbf{(TiO2)_{1-x}(Ag)_x}$ thin films with different Ag-contents determined from absorbance measurements using equation (1). The absorption coefficient of $\mathbf{(TiO2)_{1-x}(Ag)_x}$ thin films decreased sharply in the UV/VIS boundary, and then decreased gradually in the visible region because it is inversely proportional to the transmittance.[17].

$$\alpha = 2.303\frac{A}{d} \quad \text{.....(1)}$$

Where A is the absorption and (d) is the sample thickness.

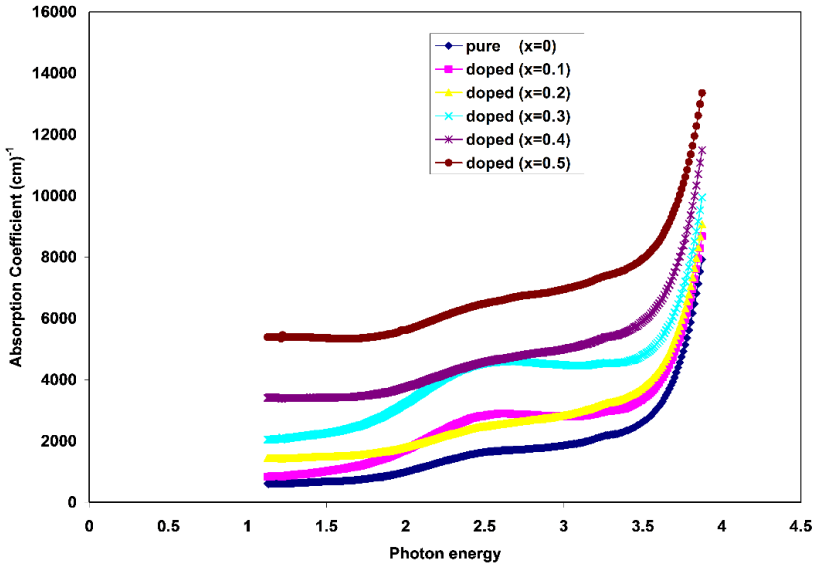

Figure (3): Absorption coefficient as a function of photon energy for $(TiO2)_{1-x}(Ag)_x$ films deposited on glass substrate with different Ag contents.

Fig. (4) Illustrates allowed direct transition electronic and the energy gap value depends on the films deposition conditions and its preparation method which influences in the crystalline structure .The variation in the structural properties and other variations is a reason for making variation in energy gap. Figures obtained for all the other thin films have a similar type of curve.The respective values of E_g is obtained by extrapolation to $(\alpha h\upsilon)^n = 0$. The E_g values for direct band gap for all the thin films are summarized in table (1). It is found in literature that $\mathbf{(TiO2)_{1-x}(Ag)_x}$ has a direct band gaps and the band gap values changes according to the preparation parameters and conditions.

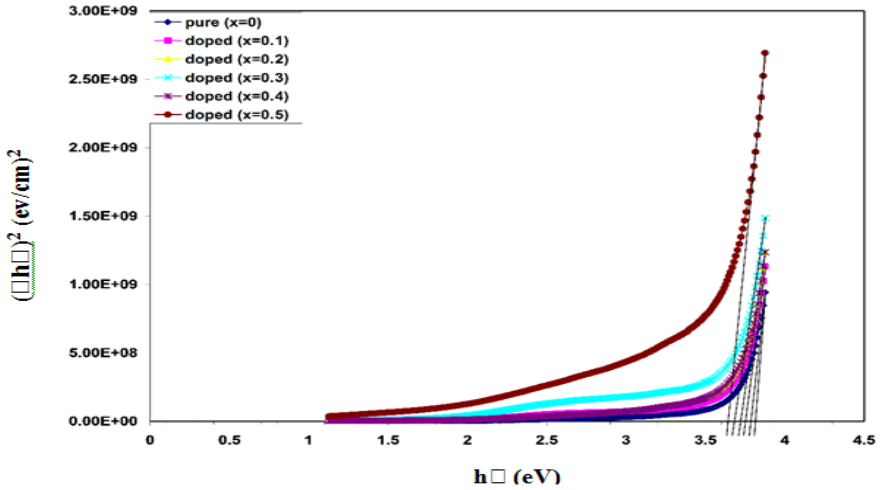

Fig. (4): Allowed direct electronic transitions of $(TiO2)_{1-x}(Ag)_x$ films deposited on glass substrate with different Ag contents**.**

From table (1) and the following fig.(4), it can be observed that (Eg) is decreasing with the increasing of doping for all films. This result is consistent with previous researches [18].Ag doping led to increased levels of localized near valence band and conduction band and these levels ready to receive electrons and generate tails in the optical energy gap and tails is working toward reducing the energy gap, or can be attributed decrease energy gap to the increased size of particles in the films, this result corresponded to wavelength absorption analysis. Not only by reducing band gap energy, but the Ag doping was also able to prevent charge recombination between electron-hole pairs. [14]

Table (1): Shows allowed direct band gap and allowed indirect band gap for different doping of $(TiO2)_{1-x}(Ag)_x$ thin films

Ag- content	Allowed direct band gap (eV)
0	3.81
10	3.78
20	3.75
30	3.72
40	3.68
50	3.63

Fig. (5) Shows the variation in refractive index of $\mathbf{(TiO2)_{1-x}(Ag)_x}$ films with wavelength. The $\mathbf{(TiO2)_{1-x}(Ag)_x}$ films deposited on glass substrate at various Ag contents for x= 0 to x=0.05.The values of the refractive index for the films at λ= 350nm vary in the range from 1.90 to 2.64 as Ag-content increased from 0 to 0.05 as are summarized in table (2). In other words, the refractive indices of the $\mathbf{(TiO2)_{1-x}(Ag)_x}$ films are increasing with Mg-content increased as shown in fig.(5).

Table (2): Shows refractive index value for different doping of $(TiO2)_{1-x}(Ag)_x$ films.

Ag- content	Refractive index
0	1.90
0. 01	2.13
0.0 2	2.18
0. 03	2.39
0.0 4	2.52
0.0 5	2.64

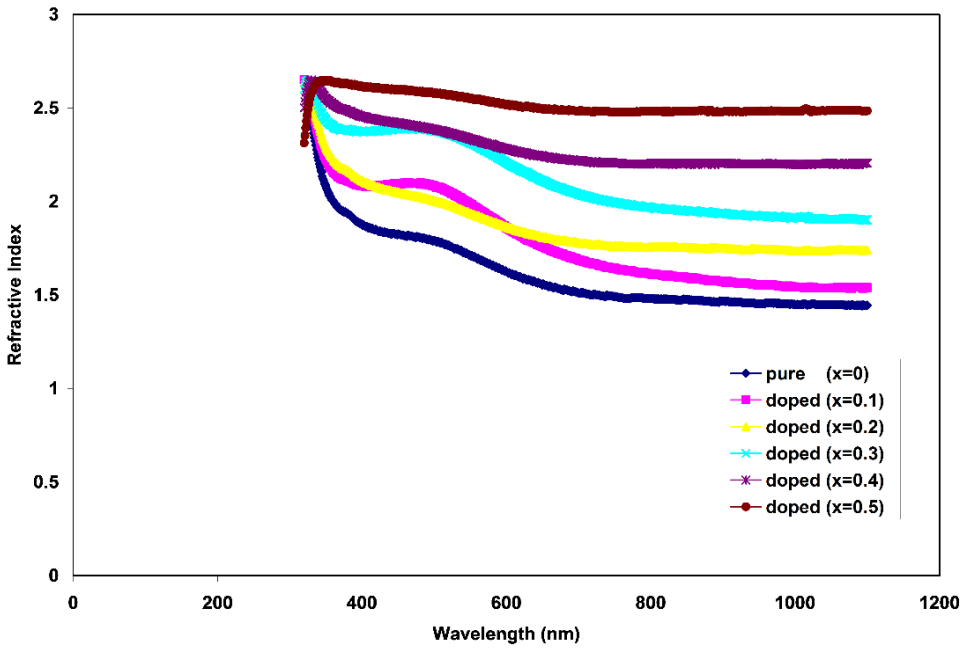

Fig. (5): Refractive index as a function of wavelength for $(TiO2)_{1-x}(Ag)_x$ films deposited on glass substrate with different Ag content.

Fig. (6) Shows the variation in extinction coefficient of **$(TiO2)_{1-x}(Ag)_x$** films with wavelength. It's clear from figure that the extinction coefficient has the same behavior absorption. The influence of doping TiO_2 of Ag concentration on the extinction coefficient values, the increasing in the extinction coefficient values with increasing the doping concentration is due to increases in the absorption, this leads to decrease the defects or the tails deep so increases in the extinction coefficient values.

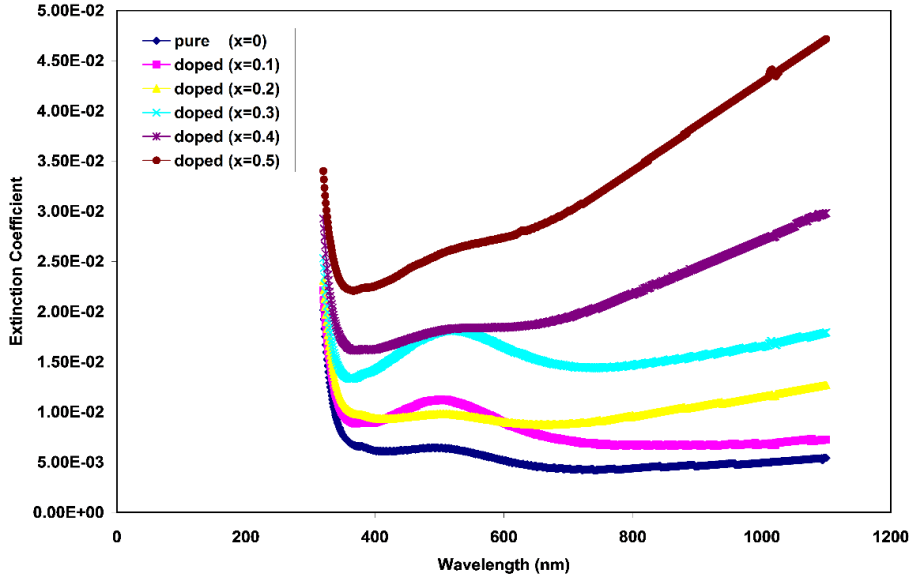

Fig. (6): extinction coefficient as a function of wavelength for $(TiO2)_{1-x}(Ag)_x$ films deposited on glass substrate with different Ag content.

The plots of real ($\varepsilon_r$and ε_i) parts of different Ag concentration for TiO_2 films are illustrated in figures (7) and (8). Our values are comparatively good to those reported earlier [19-20]. The figures show that in all samples the real part behaves like the refractive index because of the smaller value of K^2 compared to n^2, while ε_2 depends mainly on the K values, which is related to the variation of the absorption coefficient, which means the real part and the imaginary part increases when Ag contents increases. Doping TiO_2 with noble metal Ag will increase the real and the imaginary part of dielectric constants due to the increasing of the refractive index.

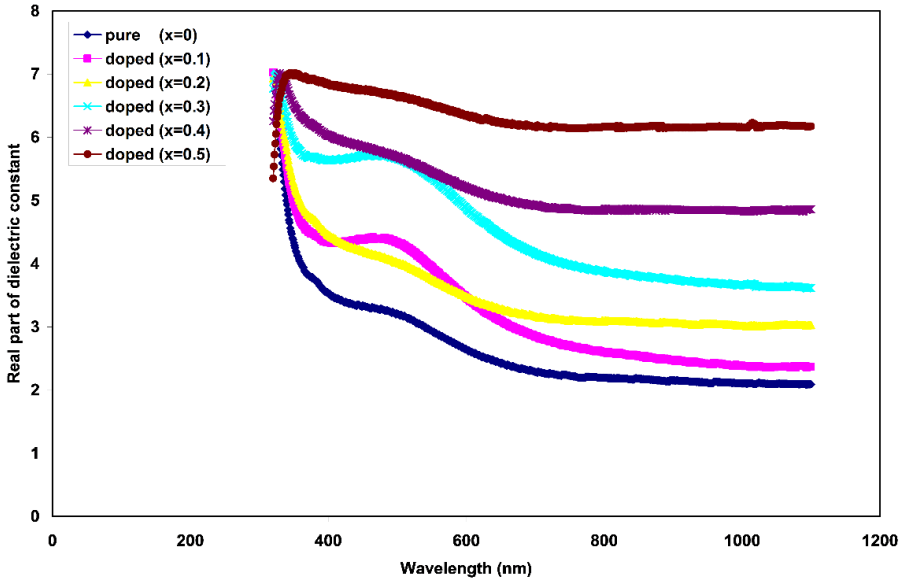

Fig. (7): Real (ε_r) parts of the dielectric function as a function of wavelength for $(TiO2)_{1-x}(Ag)_x$ films deposited on glass substrate with different Ag contents.

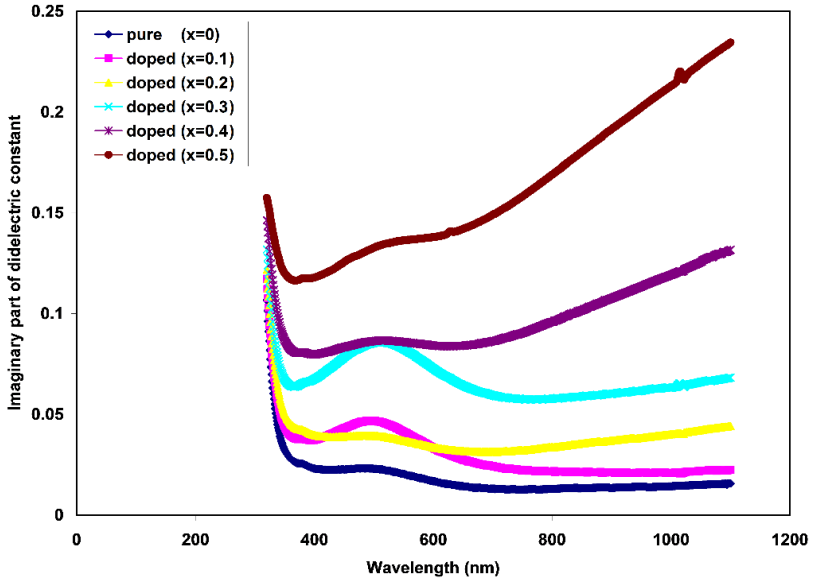

Fig. (8): Imaginary (ε_i) parts of the dielectric function as a function of wavelength for $(TiO2)_{1-x}(Ag)_x$ films deposited on glass substrate with different Ag content.

Fig. (9) Shows the variation of optical conductivity as a function of photon energy for different Ag-content of the $\mathbf{(TiO2)_{1-x}(Ag)_x}$ films. The optical conductivity is calculated by using equation (2).

$$\sigma = \frac{\alpha n c}{4\pi} \ldots\ldots\ldots\ldots (2)$$

Where (n) is the refractive index, and (*c*) velocity of light in vacuum.

From Fig. (9), we can see that the optical conductivity increases with increasing photon energy and reaches a constant value. This suggests that the increase in optical conductivity is due to electron exited by photon energy, and the optical conductivity of the films increases with increasing Ag-contents in the films.

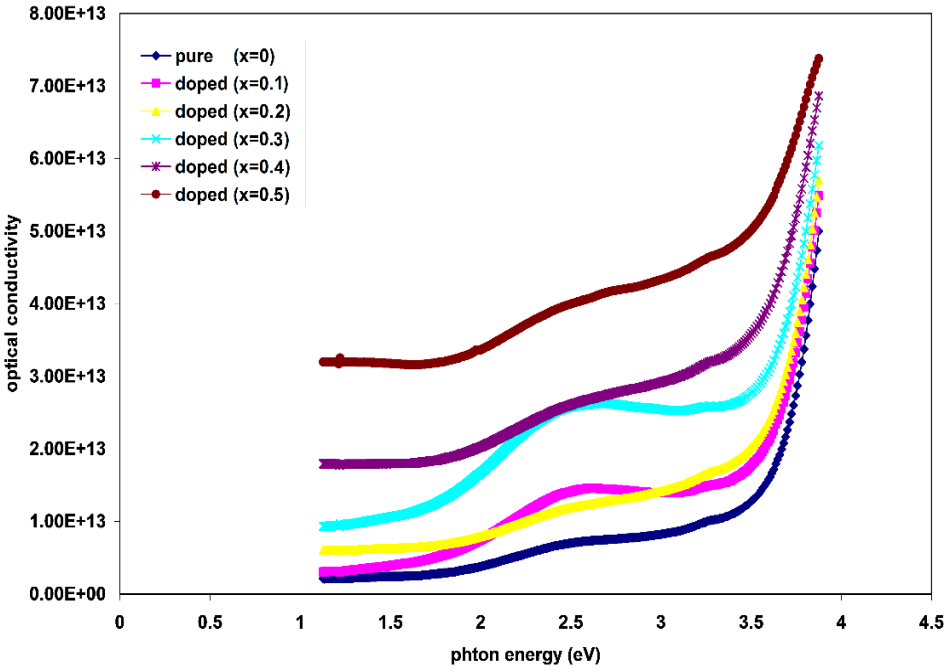

Fig. (9): Optical conductivity as a function of photon energy for $(TiO2)_{1-x}(Ag)_x$ films deposited on glass substrate with different Ag contents.

IV. Conclusions

The average transmittance for TiO_2 films is over 94% we can use these samples as an optical window in solar cell, because that TiO_2 films have average transmittance large in the wavelength range (320-1100nm) and the transmittance in UV and infrared region decreases with the increase of Ag concentration.The optical analysis showed that the influence of Ag-content on the energy gap of $Ag_xTi_{1-x}O_2$ films is significant and found that the band gap of TiO_2 could be wide anddecreases with the increase of Ag content. The observed shift in the absorption edge towards the red region clearly reflects the incorporation of Ag in the TiO_2 lattice.Also optical properties of TiO_2 thin films show that the films have allowed direct transition and allowed indirect transition. Increasing of the Ag contentfor all films cause a decrease in the optical band gap value and an increase in the optical constants (refractive index (n), extinction coefficient (K), real and imaginary parts of the dielectric constant and optical conductivity (σ)).

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